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GB 1581067 A GB 1508951 A WO 91/10547 A1
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(54) Process for preparing glass-resin prepregs

(57) This process consists in depositing on the surface of continuous glass fibres a solution comprising either one or more resins having the epoxy and acrylate groups on the same molecule, or a mixture of two or three of the following types of resin: epoxy resin, acrylate resin, or resin having the epoxy and acrylate groups on the same molecule, this solution further comprising at least one cationic photoinitiator and, optionally, a radical photoinitiator, then in subjecting the fibres to the effect of UV radiation over part of their travel.

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PROCESS FOR PREPARING GLASS-RESIN PREPREGS FOR MANUFACTURING COMPOSITE PARTS

The present invention relates to a process for preparing preimpregnated products from glass fibres and thermosetting resins for the production of composite parts by subsequent polymerisation.

It is well known that manufacturing prepregs is a complex operation requiring precise control of the conditions for its implementation and which influences the subsequent operation for the preparation of composites by total polymerisation of the prepregs, as well as the characteristics of the resultant final composites. If polymerisation should start, the resultant prepregs are unusable; likewise, if gelling is insufficient, the resultant prepregs are adhesive and present problems with respect to handling and storage.

In addition, the majority of thermosetting glass-resin composites are formed from epoxy resin. It is known from patent application FR-A-2 336 776 and the application for the certificate of addition (FR-A-2 382 079) relating thereto, to extract a glass fibre tress

from a roll, impregnating it with a mixture which is reactive to UV radiation, then gellifying and polymerising the mixture in a single step by subjecting the tress to radiation over part of its path, the reactive mixture consisting of acrylic, mono and polyunsaturated monomers, a photoinitiator forming free radicals under the effect of UV radiation, and a saturated epoxy resin.

However, in spite of the reactivity of the acrylic monomers under UV radiation in the presence of free-radical photoinitiators, the presence of the epoxy resin considerably decreases the polymerisation rate of the mixture as a function of the given irradiation time, such that it is impossible to treat the tress satisfactorily at high speeds, except by increasing the power of the irradiation source, which is not without its limitations. In this process, the mixture is thus only correctly gellified then polymerised when the tress advances at a speed of the order of 20 $m.min^{-1}$ for a UV radiation emitter tube output of 80 Watt/linear centimetre of this tube.

From the document FR-A-2 341 614 it is likewise known to deposit an epoxy resin and cationic photoinitiator-based mixture onto the

glass fibres. However, here again, the kinetics of polymerisation are very slow, owing to the presence of the epoxy resins, which has unfavourable consequences not only with respect to the speed at which the prepreg forms, but also to the use of the prepreg in the formation of composites, in which the same problems, which are due to the low reactivity of the mixture, are posed.

The first object of the invention is thus to overcome these disadvantages by establishing a rapid gellification process which overcomes the problems connected with the presence of epoxy resins.

A further object of the invention is to obtain prepregs which can polymerise rapidly in the subsequent operations for manufacturing composite parts.

The object of the present invention is likewise a rapid gellification process providing products which are suitable for manufacturing composites having good mechanical properties, irrespective of the polymerisation process used following the gellification process (by UV radiation, by electron beam or by heat treatment).

These objects are achieved in particular by rendering the impregnating resin sufficiently reactive, in spite of the presence of epoxy resins, in order to reach the gel state on glass fibres at high winding speeds (above 180 $m.min^{-1}$) during the impregnating / gellification phase under UV. One of the advantages of the invention is the increased productivity in the manufacture of prepregs as well as improved homogeneity in the thickness of the resultant final composites, in particular in the processes for manufacturing composites by winding from these prepregs.

The process to which the invention relates consists in depositing on the surface of continuous glass fibres a solution in an organic medium comprising either one or more resins having the epoxy and acrylate groups on the same molecule, or a mixture of two or three of the following types of resin: epoxy resin, acrylate resin or resin having the epoxy and acrylate groups on the same molecule, the solution further comprising at least one cationic photoinitiator and, optionally, a free-radical photoinitiator, then subjecting the fibres to the effect of UV radiation over part of their travel.

In accordance with the invention, the glass fibres may be in different forms, such as simple, unidirectional fibres, tufts, or woven or non-woven sheets.

Any type of epoxy resin can be used, in particular DGEBA (bisphenol A diglycidyl ether). In spite of their very slow cationic cross-linking kinetics, photoinitiated under UV, epoxy resins are in fact necessary for obtaining the required copolymers, and encourage the good adhesion of the coating to the glass.

Acrylate resins ensure that the mixture gels at a high speed owing to their reactivity under UV in the presence of photoinitiators which release free radicals.

The advantage of using a cationic photoinitiator is thus explained by its dual functionality. Under the effect of UV radiation, the cationic photoinitiators absorbing the energy of the radiation photons release free radicals and Lewis acids. The first react very rapidly with the unsaturated atoms of the acrylic resin, thus ensuring that gellification occurs, whilst the second react far more slowly with the epoxy groups, this second reaction assuming its full

importance during final polymerisation to produce the composites.

These reactions, which occur in two steps, are thus particularly well-suited to the production of glass fibre-based preimpregnated products, then to the manufacture of the composite itself from these prepregs.

The cationic photoinitiators used within the scope of the invention are selected from the group of compounds comprising aryldiazonium, diaryliodonium, triarylsulphonium and triarylselenium and, preferably, from the group of compounds comprising triarylsulphonium, such as triarylsulphonium hexafluoroantimoniate (marketed by the UNION CARBIDE company under the reference UVI 6974) or triarylsulphonium fluorosphosphate (marketed by UNION CARBIDE under the reference UVI 6990). Generally, these photoinitiators are used in solution in hydrogen-yielding organic solvents. Their weight content in the solution is between 0.5 and 10 % and is preferably between 3 and 5 %.

In the case of a solution comprising at least one epoxy resin and an acrylate resin but not comprising any bifunctional resin, it is further necessary to add a radical photoinitiator

such as 2-hydroxy 2-methyl 1-phenyl propane 1-one (marketed by CIBA-GEIGY under the reference Darocur (R.T.M.) 1173), 1-hydroxy cyclohexyl phenyl ketone (marketed by CIBA-GEIGY under the reference Irgacure (R.T.M.) 184) or the mixture of aromatic ketones marketed by CIBA-GEIGY under the reference Darocur (R.T.M.) 1664. Nevertheless, after gellification and polymerisation, a polymer mixture is obtained of which the mechanical properties are less good than the mixtures comprising bifunctional resin, as illustrated below in examples 1-2 and 3-4.

Thus, a mixture comprising at least one resin having the epoxy and acrylate groups on the same molecule and at least one cationic photoinitiator are preferably used. The resultant gel is then in the form of mixed prepolymers with acrylate and epoxy groups and subsequently produces copolymers having mechanical properties which are more advantageous than polymer mixtures having the same groups.

According to a particularly preferred embodiment of the invention, an epoxy resin is also used. The above-mentioned mixed prepolymers with acrylate and epoxide groups are in effect capable of subsequently cross-linking homogeneously with the epoxy molecules of the

mixture; moreover, bifunctional resin has a synergistic effect on the cross-linking of the epoxy resin and the reactivity of the epoxy groups in the mixture becomes greater than the theoretical reactivity. In this case, the mechanical properties of the composites subsequently obtained from the prepregs are far higher than in each of the other combinations.

In these mixtures, the bifunctional resin is preferably used in proportions ranging from 5 to 80 weight % so as, firstly, to allow the synergistic effect to occur and, secondly, to avoid viscosity problems associated with too high a concentration of bifunctional resin, which problems require additional heat treatments.

The prepregs produced by a process of this type can be stored for several months, possibly at low temperatures, and easily handled.

The preimpregnated products which are manufactured in accordance with the present invention may be in various forms and are suitable for manufacturing various types of composites. However, without being restricted to this particular application, the process applies in particular to the production of composite products

by winding a thread or a tuft of glass fibres preimpregnated with a solution according to the invention onto a rotating support. The glass fibres can thus be coated directly under the die plate or from rolls of the glass fibres.

In the latter case, the glass fibres are assembled in the form of a tuft of parallel fibres which is wound onto a rotating spindle and produces a roving bobbin according to a process known <u>per se</u>. The tuft is then removed mechanically from the bobbin, passes through a bath of the solution defined above, from which it emerges impregnated, then, before being wound onto a rotating support, it is subjected to the effect of UV radiation over at least part of its travel.

Prepregs are thus obtained of which the windings on the roll separate easily, the necessary gellification of the solution impregnating the tuft having been obtained with an irradiation time of only a few hundredths of a second. Kinetics of this type enable the tuft to be removed, treated and wound at speeds ranging from several tens to several hundreds of metres per minute.

When the prepregs have been stored in controlled temperature and hygrometric conditions, the composite parts are produced in the following manner.

The tufts are extracted mechanically from the rolls and wound onto a rotating support of which the shape is determined by that of the final composite product to be manufactured. Polymerisation of the resin impregnating the tuft continues during the entire winding phase and is terminated in a UV treatment, treatment with an electron beam or heat treatment. In the latter case, it may be useful to use thermal hardeners, such as the boron ethylamine trifluoride complex (marketed by CIBA-GEIGY under the reference HT 972), dianiline methylene (marketed by CIBA-GEIGY under the reference HT 972), or hexahydrophthalic anhydride (marketed by CIBA-GEIGY under the reference HT 907).

During the final polymerisation treatment, the Lewis acids released by the cationic photoinitiator during gellification of the solution react with the epoxy groups of the mixed molecule and those of the epoxy resin which may possibly be one of the constituents of the solution.

Composite products are thus obtained for direct exposure times, in particular as regards the UV treatment, which are, on average, less than one second for each winding layer, the exposure of each layer continuing, however, for the entire duration of the winding process, owing to the "transparency" of the upper layers.

Furthermore, since hardening is continuous on a revolving member, there is no longer any limitation on the thickness of the composite to be obtained by polymerisation. Thus, this process applies particularly well to the polymerisation of composites thicker than 4 mm, which limit is attained in the case of the cross-linking of composite parts under UV radiation.

It may sometimes be useful to subject the preimpregnated tuft to the effect of additional infrared radiation over part of the path which it travels between the roll and the rotating support. The aim of this light heat treatment is to lower the viscosity of the impregnating solution in order to encourage the wetting of the fibres constituting the tuft and the adhesion between adjacent turns on the rotating support.

This treatment is justified in particular when there is a high proportion of bifunctional resin of which the viscosity is high.

The following examples illustrate the advantages of the invention in a non-limiting manner.

EXAMPLE 1

In this example, the glass fibre tuft used is a tuft of R-type glass fibres, with a size of 1600 tex, each fibre consisting of filaments of which the average diameter is 14 µm. The tuft is impregnated by a diaphragm metering pump. The average rate at which the tuft is coated is 22 weight %.

The organic solution deposited on the tuft has the following composition, expressed as weight percentages:

- epoxy prepolymer (DGEBA) marketed by SCHELL under the reference EPON 828 — 38.7 %
- epoxy / acrylate prepolymer (partially acrylated DGEBA) marketed by U.C.B. under the reference EBECRYL (RTM.) 3605 — 59 %

- cationic photoinitiator 2.2%
  triarylsulphonium hexafluoroantimoniate
  marketed by UNION CARBIDE
  under the reference UVI 6974

The photoinitiator is dissolved in propylene carbonate in a proportion of 50/50. The winding speed is 360 $m.min^{-1}$.

The impregnated tuft is subjected to the radiation emitted by a 25 cm long mercury vapour tube having an output of 60 Watts per linear centimetre of tube. An elliptical reflector at the rear of the tube causes the rays to converge on the tuft passage. The conversion rate measured after gellification is between 11.3 % and 23.1 % for the acrylates and 2.3 % and 6.8 % for the epoxys, the total conversion being of the order of 3 to 8 %.

The resultant tuft is then used in the following conditions. The tuft, extracted mechanically from a roll, is wound in the form of a ring onto a rotating support, after being tensioned by rails used as a brake. Between these rails and the support, the tuft passes through an oven of which the temperature is of the order of 250°C. The winding speed is 12 $m.min^{-1}$.

The tuft in the process of being wound onto the support is subjected to the UV radiation emitted by a 25 cm long mercury vapour tube having an output of 120 Watts per linear centimetre of tube. At the rear of the tube, a reflector causes the rays to converge. The UV radiation source is placed at a sufficient distance from the support to define on its surface an irradiation zone with a width of the order of 40 mm.

The resultant conversion rate after final polymerisation is of the order of 100 % for the epoxy resins and 55 % for the acrylates, the total conversion being of the order of 95 %. In addition, the interlaminar shearing stress of the resultant composite product on the NOL ring is 59 MPa.

EXAMPLE 2

In this example, a composite product is produced according to the same method as described above in example 1, from a tuft of glass fibres coated with an organic solution having the following composition, expressed as weight percentages:

- epoxy prepolymer 76.4 %

(DGEBA) marketed by SCHELL under
the reference EPON 828

- diacrylate oligomer marketed by HARCROS under the reference PHOTOMER (RTM) 3016 — 14.4 %
- trimethyl-ol-propane triacrylate marketed by U.C.B. under the reference TMPTA — 4.8 %
- cationic photoinitiator triarylsulphonium hexafluoroantimoniate marketed by UNION CARBIDE under the reference UVI 6974 — 3.4 %
- radical photoinitiator 2-hydroxy 2-methyl 1-phenyl propane 1-one marketed by CIBA GEIGY under the reference DAROCUR (R.T.M) 1173. — 1.0 %

The interlaminar shearing stress of the resultant composite product on the NOL ring is 40 MPa.

The mechanical properties of the composite products obtained according to the invention using an impregnating solution containing a bifunctional resin and an epoxy resin in the presence of a cationic photoinitiator are thus better than those of composite products obtained according to the invention using a

mixture of epoxy resin and acrylate resin in the presence of a cationic photoinitiator and a radical photoinitiator (example 1).

EXAMPLE 3

In this example, a preimpregnated product is produced according to the same method as described above in example 1, from a tuft of glass fibres coated with an organic solution having the following composition, expressed as weight percentages:

• epoxy prepolymer (DGEBA) marketed by SCHELL under the reference EPON 828	38.1 %
• epoxy /acrylate prepolymer (partially acrylated DGEBA) marketed by U.C.B. under the reference EBERCRYL (R.T.M.) 3605	57 %
• thermal hardener boron fluoride ethylamine complex marketed by CIBA GEIGY under the reference HT 973	2.9 %
• cationic photoinitiator triarylsulphonium hexafluoroantimoniate marketed by UNION CARBIDE under the reference UVI 6974.	3.4 %

The resultant tuft is then used to produce a composite product by winding the tuft onto a rotating support, polymerisation of the resin impregnating the tuft being continued and terminated by a heat treatment at 160° C for 4 hours. The winding speed is 360 $m.min^{-1}$.

The interlaminar shearing stress of the resultant composite product on the NOL ring 63 MPa.

EXAMPLE 4

In this example, a composite product is produced according to the same method as described above in example 3, from a tuft of glass fibres coated with an organic solution having the following composition, expressed as weight percentages:

• epoxy prepolymer (DGEBA) marketed by SCHELL under the reference EPON 828	74.7 %
• diacrylate oligomer marketed by HARCROS under the reference PHOTOMER (R.T.M.) 3016	14.0 %

- trimethyl-ol-propane triacrylate marketed by U.C.B. under the reference TMPTA — 4.7 %
- thermal hardener boron fluoride ethylamine complex marketed by CIBA GEIGY under the reference HT 973 — 2.8 %
- cationic photoinitiator triarylsulphonium hexafluoroantimoniate marketed by UNION CARBIDE under the reference UVI 6974 — 2.8 %
- free-radical photoinitiator 2-hydroxy 2-methyl 1-phenyl propane 1-one marketed by CIBA GEIGY under the reference DAROCUR (R.T.M.) 1173. — 1.0 %

The interlaminar shearing stress of the resultant composite product on the NOL ring is 54 MPa.

COMPARATIVE EXAMPLE

In this example, a composite product is produced according to the same method as described above in example 3, from a tuft of glass fibres coated with an organic solution having the following composition, expressed as weight percentages:

- epoxy prepolymer (DGEBA) marketed by SCHELL under the reference EPON 828 — 76.2 %
- diacrylate oligomer marketed by HARCROS under the reference PHOTOMER (R.T.M.) 3016 — 15.2 %
- trimethyl-ol-propane triacrylate marketed by U.C.B. under the reference TMPTA — 5.1 %
- thermal hardener boron fluoride ethylamine complex marketed by CIBA GEIGY under the reference HT 973 — 2.3 %
- free-radical photoinitiator 2-hydroxy 2-methyl 1-phenyl propane 1-one marketed by CIBA GEIGY under the reference DAROCUR (R.T.M.) 1173. — 1.2 %

The interlaminar shearing stress of the resultant composite production the NOL ring is 52 MPa.

The mechanical properties of the composite products obtained according to the invention are as good as, if not better than, the mechanical characteristics of the composite products obtained under the same conditions from prepregs according to the prior art.

It should be repeated that these examples are non-limitative. The process according to the invention can be applied to the manufacture of various types of prepregs in the form of tufts, sheets or shaped articles. The composites obtained from these prepregs can be, for example, tubes, containers, reservoirs, tanks, etc.

CLAIMS

1. Process for manufacturing thermosetting glass - resin preimpregnated products, which consists in depositing on the surface of continuous glass fibres a solution in an organic medium comprising either one or more resins having, on the same molecule, epoxy and acrylate groups, or a mixture of two or three of the following types of resin: epoxy resin, acrylate resin, and resin having epoxy and acrylate groups on the same molecule, this solution further comprising at least one cationic photoinitiator and, optionally, a free-radical photoinitiator, then in subjecting the fibres to the effect of UV radiation over part of their travel.

2. Process according to Claim 1, characterised in that the solution contains between 5 and 80 % of a resin having the epoxy and acrylate groups on the same molecule.

3. Process according to Claim 2, characterised in that the solution contains an epoxy resin.

4. Process according to Claim 1, characterised in that the solution contains an

epoxy resin and an acrylate resin as well as a cationic photoinitiator and a radical photoinitiator.

5. Process according to any one of Claims 1 to 4, characterised in that the photoinitiators used are selected from the group of compounds comprising aryldiazonium, diaryliodonium, triarylsulphonium and triarylselenium.

6. Process according to Claim 5, characterised in that the photoinitiators are selected from the group comprising triarylsulphonium compounds.

7. Process according to any one of the preceding claims, characterised in that the fibres are impregnated with a solution of which the weight content of cationic photoinitiator is between 0.5 and 10 % and is preferably between 3 and 5 %, the photoinitiator (s) being in solution in a hydrogen -yielding organic solvent.

8. Process according to any one of the preceding claims, characterised in that the fibres are extracted mechanically from a roll, they are brought into contact with the solution, they are wound onto a rotating support, and they are

subjected to the effect of UV radiation over at least part of their travel before being wound.

9. Process according to Claim 8, characterised in that the irradiation time is of the order of a few hundredths of a second.

10. Process according to either one of Claims 8 and 9, characterised in that the fibres are extracted mechanically from the previously produced roll, they are wound onto a rotating support, and they are subjected to a UV radiation treatment, electron beam treatment or a heat treatment on the support during the winding operation and, optionally, in the presence of a thermal hardener.

11. Process according to Claim 10, characterised in that the fibres are subjected to the effect of infrared radiation over at least part of the path travelled by the fibres between the roll and the support.

12. Process according to either one of Claims 10 and 11, characterised in that the UV radiation process is performed for the entire winding process, each layer being directly exposed to the

radiation for an average duration of less than one second.

13. Application of the process as defined in any one of Claims 10 to 12 to the production of composites.

14. Application of the process as defined in any one of Claims 10 to 12 to the production of composites, the composites being polymerised over thicknesses of more than 4 mm under UV radiation.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
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Relevant Technical Fields

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(ii) Int Cl (Ed.5) C08J 5/00, 5/04, 5/08, 5/10, 5/24

Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES : WPI

Search Examiner
ALEX LITTLEJOHN

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15 FEBRUARY 1994

Documents considered relevant following a search in respect of Claims :-
1-14

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
Y	GB 1581067	(EHRNFORD) - see whole document, eg page 1 lines 73-93	1, 3, 5, 6, 13
Y	GB 1508951	(CIBA-GEIGY) - see whole document, eg page 3 lines 6-12 and page 4 lines 8-27	1, 3, 5, 6
Y	US 4227978	(BARTON) - see whole document eg columns 5-7	1, 3, 5, 6, 13
Y	US 4156035	(TSAO) - see whole document eg column 2 lines 38-49	1, 3, 5, 6, 13
X	WO 91/10547 A1	(FREEMAN) - see whole document, especially page 6 lines 21-23 and Example 7 on page 15	1-3, 13
Y	WO 87/05540 A1	(DESOTO) - see whole document, eg page 2 lines 12-28	1, 3, 5, 6, 13

Databases:The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).